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Reliable and reproducible determination of work function and ionization potentials of layers and surfaces relevant to organic light emitting diodes

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Abstract

Ultra violet photoelectron spectroscopy has been used in most of the research related to determination of the energy levels of the materials in multilayer devices, such as organic light emitting diodes, to measure the Fermi and HOMO levels of conductors and organic materials, respectively. The variation in the values reported in the literature often remains unexplained despite apparently similar experimental conditions. We report (i) on the methods that we have found are required to achieve reproducible and stable values of work function (WF) and ionization potentials (IP) of ITO and common organic layers, and (ii) on the origin of the variations. Not unexpectedly, we have found that hydrocarbon contamination arising from vacuum pumps (e.g. oil diffusion pumps) can cause significant changes in WF or IP. Of greater possible significance is the observation that continuous exposure to ultraviolet light can enhance these effects and can change the work function of an interface much faster than would occur in the absence of UV light. The major effect probably arises from effects of the secondary electrons produced by the 21.22 eV photons of the He resonance lamp. By dealing with these problems, we have been able to measure stable values for WF and IP over extended periods of time ranging from hours to days.

Keywords: Work function; Ionization potential; Vacuum level

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1. Introduction

The reliable and reproducible measurement of work function (WF) and ionization potentials (IP), for conductors and organics, respectively, has always been challenging. Ishii and Seki's clarification [1] of the role of the vacuum level shift at the organic/metal and organic/organic interfaces has been a major improvement in the conceptual understanding of the interfacial energy level structure of multilayer devices. The measurement is apparently quite routine and essential in many areas of research, in addition to the organic light

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emitting diode (OLED) and semiconductor industries. Reliable information is crucial for progress in the fabrication of OLED devices, in which understanding of the energy levels in the various materials plays a key role in moving from a simple structure to a complicated multilayer device structure. OLEDs have evolved from a simple single organic layer to a multilayer structure involving the hole transport layer (HTL), electron transport layer (ELT), hole injection buffer layer, electron injection buffer layer, and so on. Accurate knowledge of the energetics of charge injection from the electrodes and of the energy barrier(s) to charge flow through the multiple interfaces, is required for rational design of an OLED.

Ultra violet photoelectron spectroscopy (UPS) has been used in the majority of published research for the determination of energy levels. Photoemission spectroscopy is intrinsically surface sensitive and UV excited spectra allow direct access to the valence electrons involved in bonding. Laboratory sources restrict UPS to studies of levels within a few 10s of eV of E_f but the cross-sections for photoemission are much larger than for X-rays, resulting in much greater signal intensity in UPS compared to X-ray excited valence band spectra. In most surface science laboratories, UV photons are produced using inert-gas plasma discharge lamps and the kinetic energies of the emitted electrons can be calculated from the following equation:

$$E_k = hv - E_\mathrm{b} + \Delta\phi,$$

where E_k is the electron kinetic energy, hv is the energy of the incident photon, E_b is the electron binding energy, and $\Delta\phi$ is the difference in WFs between the sample and the detector material assuming that there is no electrical charging at the sample surface. The highest E_b measurable by UPS is given by $hv - \Delta\phi$. Practically, the zero of the binding energy ($E_\mathrm{b} = 0$) scale is set at the Fermi level, and this is our practice. In our system, the light source is a He-resonance lamp [2] producing HeI (21.22 eV) and HeII (40.81 eV) radiation at a discharge pressure of He of about 8×10^{-2} Torr. By means of two stages of differential pumping of the source, the pressure in the main chamber can be maintained at about 10^{-7} Torr during operation; most of this is He and does not present a contamination problem because we use research grade purity He gas (99.999%) which is passed through a LN_2 cooled zeolite filled trap. We demonstrate below that either the effect of UV irradiation or the *combination* of UV irradiation *and* gaseous contaminants can produce significant effects on OLED interfaces.

As mentioned above, UPS is widely used by OLED research groups to measure the energy levels in multilayer structures. Table 1 contains literature data for the WF of ITO, and for the IPs of organic materials. While this is not a comprehensive survey, Table 1 illustrates the very large discrepancies in the published data. Many explanations have been advanced for these discrepancies based on different treatment of the materials or even the suggestion that different sources of ITO have different work functions. Certainly there are differences in surface topography from different suppliers, and it is important that the surface stoichiometry be reproducible from lab to lab. The latter property will depend upon the cleaning treatments used. In our work we have found two major sources of variation in our experimentally determined WFs and IPs that might be relevant to the discussion. They are, first, the use of "wet" pumps such as oil diffusion pumps, even when UHV conditions are obtained and, second, deg-

Table 1
Reported values for WF for ITO and IP for typical organic materials used in OLEDs

ITO	NPB[a]	Alq_3[b]	CuPc[c]
<4.8 [7]	5.4 [8]	5.7 [8]	4.8 [15]
<4.7 [8]	5.2 [15]	5.6 [9]	5.0 [17]
4.75 [10]	5.7 [11]	5.85 [11]	4.7 [13]
4.5 [12]	5.1 [13]	5.7 [15]	4.95 [14]
4.3 [15]		5.9 [1]	5.3 [16]
4.4 [17]		5.7 [18]	
4.4 [19]		5.9 [20]	
4.8 [21]		5.35–5.56 [22]	
		5.93 [23]	
		6.1 [24]	

[a] *N*,*N*′-bis-(1-naphyl)-*N*,*N*′-diphenyl-1, 1′-biphenyl-4, 4′-diamine.

[b] Tris(8-hydroxyquinoline)aluminum.

[c] Copper phthalocyanine.

radiation of the surface by radiation from the UV source.

2. Experimental

We carried out the measurements in a multichamber UHV system capable of fabricating producing thin films and devices, treating them in chosen ways and of testing and analyzing them in situ.

The conductive glass samples of ITO films deposited on Float Glass were supplied by Delta Technologies. The substrates were cut from pieces with a sheet resistivity of 10 Ω/□. We also used some ITO substrates of similar resistivity from Magna Donnelly, to compare with the above. Our substrates were initially degreased by scrubbing in detergent (Liqui-Nox®) and deionized water and then were cleaned by ultrasonic agitation successively in deionized water and detergent, deionized water, methanol, isopropyl alcohol, and distilled acetone for 15 min each. The sample was then loaded into the load-lock chamber and was UV-ozone treated prior to evacuating the chamber assuring that the substrate was not exposed to atmosphere between ozone treatment and placement in vacuum. The films were fabricated at a base pressure of 2×10^{-8} Torr.

Evaporation rates and also film thicknesses were checked by a calibrated quartz crystal monitor. The organic materials were supplied and purified by Xerox Research Center of Canada. The organic thin films were deposited on ITO substrates from buffered tantalum heating boats at rates ranging from 2 to 6 nm/min. Energy level measurements were carried out in the analysis chamber connected to the evaporation chamber allowing in situ measurements. This chamber is equipped with a turbo-molecular pump and a titanium sublimation pump providing a base pressure of better than 2×10^{-10} Torr. While all chambers are usually pumped in a dry environment (turbo-molecular pump), they are also connected to diffusion pumps with liquid nitrogen traps. These diffusion pumps were used to investigate their effect on surface properties. From now on we will use the term "type 1 vacuum" for chambers pumped by a combination of diffusion pump and titanium sublimation pump and "type 2 vacuum" for chambers pumped by a combination of turbo-molecular pump and titanium sublimation pump.

The HeI line at 21.22 eV was used as the excitation source for UPS. The organic materials utilized in this study have a good surface conductivity in the range of film thickness used for the UPS measurement so charging is not a problem. The resolution of the UPS measurements was ≈200 meV, as determined from the width of the Fermi edge of a very pure Ni plate cleaned in situ by ion-sputtering, and changes in WFs and IPs could be determined to about ±50 meV. The samples were biased at −12 V dc to permit the separation of the secondary electrons cut-offs from the sample and spectrometer which otherwise overlapped; this then permitted the determination of the vacuum level [1] of the sample in the manner discussed by Ishii and Seki [1]. Sputtered clean polycrystalline nickel and also in situ evaporated Al films were used to find the Fermi level as the reference for ITO. Organic films thicker than 10 nm were used to measure IPs.

3. Results

We investigated two major causes for variations in measured values for WF and IP: the vacuum environment produced by different pumping systems, and prolonged UPS measurement of the measured values of energy levels. In the investigation of the effect of vacuum ambient, the WF was determined periodically by UPS, and the time during which the samples were exposed to the UV beam was kept to a minimum.

3.1. Work function variation with treatment and vacuum conditions

A combination of baking, diffusion pumping, liquid nitrogen cold trap and LN_2 cooled titanium sublimation pump (type 1 vacuum), produced and maintained the base pressure in the 10^{-10} Torr range. Mass spectrometer analysis of the ambient showed the presence of hydrogen, CO, H_2O and

CO_2 and very small amounts of ions which were best attributed to the cracking of higher molecular weight hydrocarbons. The quadrupole mass spectrometer used had limited sensitivity for masses for which $m/e > 100$. Typically it has been assumed that such a vacuum will permit storage of a sample of ITO or exposed organic layers for significant times without change in WF or IP; this assumption arises from the belief that an ambient which consists of gases such as CO, H_2, CO_2, etc. which are easily detectable by quadrupole mass spectrometers, should not interact strongly with ITO or the organic layers. Low ambient pressures of these species is not a sufficient criterion, as we demonstrate below for the diffusion/sublimation pump combination ("type 1 vacuum"), even though the indicated vacuum is in the low 10^{-10} Torr region. Very low ambient pressures of hydrocarbons can cause contamination over periods of hours or days. Gas kinetic theory shows that partial pressures of molecules that could *condense* on a surface must be in the 10^{-11}–10^{-12} Torr range to ensure clean surfaces over periods of days for molecular weights of ~100 Daltons or more.

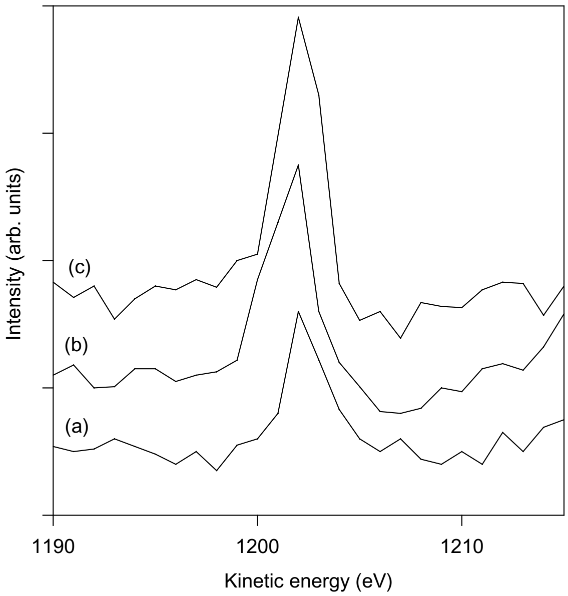

Fig. 1. XPS spectra of ITO showing carbon 1s core-level: (a) right after the clean ITO was introduced into the vacuum chamber, after staying in type 1 vacuum of 5×10^{-10} Torr for (b) 4 h and (c) 1 day.

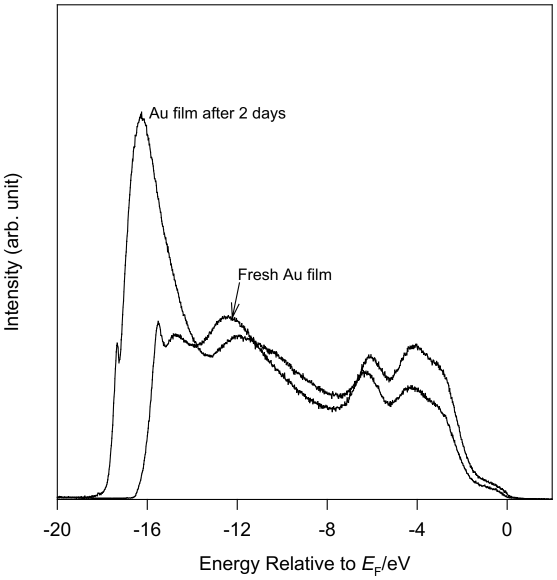

Fig. 2. HeI UPS spectra of freshly ion sputtered Au and after 2 days in UHV type 1 vacuum.

In type 1 vacuum and UV lamp off, the ITO WF typically decreased slowly by 0.2–0.6 eV over a period of ~1 day depending on the chamber pressure but still in the UHV regime. XPS of the C 1s peak showed the continual accumulation of carbon on the surface (Fig. 1). This effect was confirmed through measurements of the WF of a freshly sputtered gold sample. Fig. 2 shows that the WF of Au decreased by about 1 eV after being left in type 1 vacuum for 2 days with the pressure kept around 5×10^{-10} Torr and the lamp off. By contrast, the same gold plate showed a decrease in WF of only ~0.15 eV over the same period while the lamp was kept off and in a type 2 vacuum environment, even though the total pressure indicated by an ion gauge was similar. XPS measurements of the C1s signal showed no significant change in carbon contamination after this elapsed time. The conclusion must be that there is a larger background of hydrocarbons in the diffusion pumped system, even though these were not readily measured by a quadrupole mass spectrometer. For reasonable values of molecular weight, sticking coefficient and work function change per monolayer, the results in type 1 vacuum would be consistent with partial pressures of condensable hydrocarbons of ~10^{-11} Torr, while the partial pressures in type 2 vacuum were a factor of up to 10 less than this.

To test for the presence of hydrocarbons in the He flowing through the resonance lamp, we periodically monitored the WF and IP of the sample after positioning the sample either directly in the He gas beaming from the lamp capillary, or removed from direct beaming effects *with the lamp off*. In neither case did we see any significant change in WF and IP. This is not surprising as the He used is of 99.9999% purity and is passed through a LN_2 cooled zeolite-filled trap. The effective pressure of He at the sample is ~10^{-7} Torr, and hence any impurities brought in with the He should be present at pressures below 10^{-13} Torr.

3.2. Effect of irradiation

In a typical UPS measurement in many labs, the sample is loaded into the chamber, positioned in front of the lamp, and the UPS spectrum acquired for a certain time to obtain adequate S/N ratio. We observed that an extended measurement duration affects the measured values for WF and IP drastically. Fig. 3 shows the variation in ITO WF versus time of UV irradiation in both types 1 and 2 vacua. There is a sharp decrease within the first hour that slows down and reaches saturation after a few hours. The change in WF by UV irradiation is slower in type 2 vacuum but still comparable to that in type 1. Interestingly, the original WF value in both cases was restored after UV ozone treatment. This observation along with the increase in the amount of carbon on the surface (verified by XPS) proves that the decrease in WF in type 1 vacuum must be at least partially attributed to the accumulation of carbon which can be removed by the UV ozone treatment. Changes in WF under X-rays irradiation have been reported in the literature, so the XPS measurements used to confirm the presence or absence of carbon contamination were carried out only after the WF measurements by UPS, and the measurement duration kept to ~10 minutes using non-monochromated AlKα X-rays.

There remains the possibility that the effect on the WF of ITO under irradiation even in type 2 vacuum, results from contamination that arises within the lamp itself during operation when its internal structures get very hot; this contamination, once released from the walls of the lamp, would be carried in the beam of He directly to the surface. We tested for this possibility by continuous irradiation of a clean gold sample; the change in work function was the same as that which occurred sitting in a type 2 vacuum in the absence of UV irradiation.

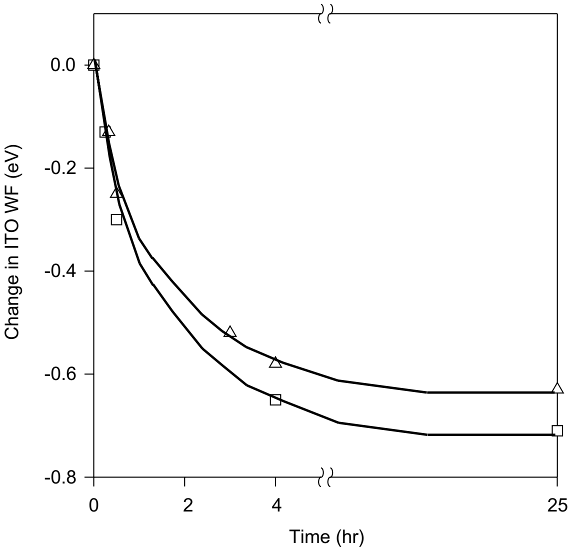

Fig. 3. Variation of ITO WF by time; (□) for ITO in type 1 vacuum and irradiated by UV source, (△) for ITO in type 2 vacuum and irradiated by UV source. The *x*-axis shows the elapsed irradiation time.

The easy reversibility of the changes in work function by ozone treatment is in contrast to other treatments such as ion sputtering [10] and plasma [3,4,10] or aggressive chemical treatments [5,19] which can result in permanent changes to the surface. As far as we can tell from published reports, many UPS measurements involve prolonged UV irradiation and storage in vacuum, and cleaning procedures such as ion or plasma treatments.

3.3. Ionization of organic materials

Table 2 lists our measurements of the difference in IP for some common organic materials used in OLEDs determined under the two different

Table 2
Difference in IP for common organics used in OLEDs using two different measurement techniques

Organic material	IP, type 1 vacuum, prolonged irradiation (eV)	IP, type 2 vacuum, minimal irradiation (eV)
CuPc	5.02	5.20
NPB	5.35	5.70
Alq_3	5.60	6.15

(extreme) conditions: type 1 vacuum with prolonged irradiation, and type 2 vacuum with minimal irradiation time (just sufficient to determine the WF or IP). The effect of the two mentioned factors is small on CuPc, significant for NPB, and large for Alq_3. Use of a type 2 vacuum (clean and "dry") and minimization of the UV exposure enabled us to produce surfaces with *reproducible and stable* measured WF and IPs for extended periods of up to a few days. Different samples from the same batch of ITO or organics yielded very similar WF and IPs. This means the data we have presented in this article are reproducible and do not change from day to day or slight difference in preparation. We therefore regard these values as representative of uncontaminated and stoichiometric surfaces.

4. Discussion

The observed variations in ITO work function reported in the literature have often been attributed to differences in the supplier, or to differences in the thickness or other characteristics of the particular ITO sample. However, with the precautions listed in this report, our measurements of the WF of different ITOs showed no significant variations, lying in the range from 5.2 to 5.4 eV.

The effects of UV irradiation on ITO are particularly interesting and important, and might well offer a rationalization of the range of values of the WF of ITO reported in the literature. We have conclusively demonstrated that the work function of a freshly prepared ITO surface which exhibits an initial work function of ~5.3 eV, decreases by ~0.6 eV under UV irradiation with 21.22 eV photons, and that almost none of this effect in type 2 vacuum is attributable to contamination. We speculate that the effect is due to the ejection of oxygen ions from the ITO surface under irradiation, most probably via the influence of the energetic secondary electrons. The ejection of oxygen ions from oxide surfaces under irradiation is a well known phenomenon [6]. Presumably, it is the removal of negatively charged oxygen ions from the surface that leads to the decrease in WF. Our results might thus provide a rationalization of the reported discrepancies in values of WF and IP of ITO and organic materials in the literature. In particular, care must be taken to keep the total photon fluence as low as possible in the UPS measurements. For the best signal to noise it is therefore necessary to use a spectrometer of the highest possible transmission and sensitivity, rather than extended data accumulation.

One further effect that is worth noting in such measurements in a type 1 vacuum, is the observation that hydrocarbon contamination, as judged by the accumulation of carbon on the surface of a clean gold sample, was more rapid under UV irradiation, even though we know the lamp is not the source of the contamination. The most plausible explanation is that hydrocarbons condensing on a surface are rapidly converted to an irreversibly adsorbed form (physisorbed to chemisorbed, or via dissociation) by the UV light and/or secondary electrons. The hydrocarbons formed on the surface during the irradiation can easily be removed by a soft technique like UV-ozone treatment.

5. Conclusions

We have identified significant experimental problems in UPS measurements of electronic energy levels, in particular when sensitive samples are investigated. Significant variation in the WF of ITO and the IPs of common organic materials used in OLEDs were traced to the effects of vacuum environment and prolonged UV irradiation. When care is taken to eliminate or minimize these effects, reproducible and stable values can be obtained for periods of up to days and on samples from different sources. In the case of ITO, careful washing and use of UV-ozone treatments produce highly reproducible surfaces. Reliable values of WF and IPs are essential for any band picture of OLED and some of the variations reported in the WFs and IPs in the literature might be due to these effects.

Acknowledgements

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